IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of Yuki ISEKI, et al.

Serial No. : 10/809,928 Group Art Unit : 1713

Filed : March 26, 2004 Examiner : Rip A. Lee

For : ETHYLENE COPOLYMER

* * * * * *

DECLARATION UNDER 37 C.F.R. §1.132

Honorable Commissioner of Patents and Trademarks

Washington, D.C. 20231

Sir:

I, Yuji SHIGEMATSU, a Japanese citizen residing at 4-10-18-1606, Toyosu, Koto-ku, Tokyo, Japan, declare:

That I graduated from Department of Material Chemistry, Faculty of Engineering of Yokohama National University, in March 1987, and graduated master course of Graduate School of Material Science, Yokohama National University in March 1989, entered Sumitomo Chemical Company, Limited in April 1989, and in the First Laboratory of Chiba Laboratories of said company,

That I had been engaged in study regarding properties and structures of ethylene polymers, production process of novel ethylene polymers, techniques of processing and evaluation of

ethylene polymers and applications of ethylene polymers in the First laboratory from then to January 1995;

That I had been engaged in development of processing techniques of extruded resins in Resin Development Laboratory of said company between January and September of 1995;

That I had been engaged in domestic marketing of polystyrene in department of Polystyrene(Osaka), Synthetic Rubber-Polystyrene Division of said company from October, 1995 to September, 1997;

That I had been engaged in domestic marketing of polystyrene in Osaka Branch of Japan Polystyrene Inc. from October, 1997 to July, 2003;

That I had been engaged in domestic marketing of polyethylene in department of Industrial Material of Sumitomo Mitsui Polyolefin Company, Limited between August and September of 2003;

That I have been engaged in domestic marketing of polyethylene in department of Industrial Material, Polyethylene Division of Sumitomo Chemical Company, Limited since October, 2003;

That I am one of the inventors of EP 0 640 627 A1 cited in the office action mailed on July 7, 2005 of the above-identified application;

That I conducted analysis of ethylene polymer samples including a sample of VIB196 and prepared a monthly research report(1) of December of 1992 (reporting Date: December 28, 1992) attached hereto, proviso that descriptions which have no relation to VIB196, were omitted or black-lacquered;

That I received from Yuji KANDA (who is also one of the inventors of EP 0 640 627 A1, but not enrolled at Sumitomo Chemical Company, Limited now) a report in which the relaxation time (equal to T99) of VIB196 was 3.63 second as described in KANDA's monthly research report(2) of January in 1993(reporting

Date: January 28, 1993), attached hereto;

That I believe that VIB sample is as follows:

(1)VIB196 was produced under conditions described in Table 4 of the report(1), therein, TN-4 and DEAC as Y catalyst and BEM as X catalyst are respectively $[(C_8H_{17})_2N]_4Ti]$ and Diethyl aluminum chloride, and butyl ethyl magnesium used in Example 1 of EP 640 627A1 cited, and

(2)Properties of VIB196 are as described in Table below:

Properties	Unit	VIB196
MFR	g/10 min.	2.85
Relaxation time(τ)	Second	3.63
Melt tension(MT)	cN	3.3
Activation energy of flow (Ea)	kJ/mol	44.5
Density	g/cm^3	0.9275

That I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above identified application or patent issued thereon.

Signed this 16th day of December, 2005.

Yuji Shigematsu

Yuji SHIGEMATU

1月度研究月報 H5－1－28

神田

ポリエチレンの構造と物性に関する研究
TN触媒重合PEの動的粘弾性挙動

1、序

今月度はTN触媒を用いたslurry法および、HIP法により得られたPE、さらに、Ti系メタロセン触媒重合PEについて動的粘弾性の周波数依存性を測定し、今までに得られた種々のプロセスで製造されたPEと粘弾性挙動の相違について比較した。

2、実験

（試料）

試料名	プロセス	Me/1000C	MFR	MFRR
PTN－44	TN-4/DEAC/BEM(slurry)	18.2	0.41	31.4
PTN－71	ﾒﾀﾛｾﾝ/DEAC/BEM	20.8	0.34	35.4
[redacted]	TN-4/DEAC/BEM(HIP)	14.9	2.85	45.1

ﾒﾀﾛｾﾝ：Cp2Ti（NOct2）2

（測定）

1)動的粘弾性の周波数依存性

RMS－800 parallel plate strain：20％

温度：130℃→250℃（temp-freq. sweep）

周波数：100→~~0~~ 0.1 rad/sec

2)応力緩和試験

parallel plate, strain：20％ ,

温度：130℃

3、結果、考察

（表3－1） …PTN－44、71、VIB－197の粘弾性挙動のまとめ

（図3－1） …PTN－44、71、VIB－197130℃におけるη^*の周波数依存性曲線（130℃）

（図3－2～4）…PTN－44、71、VIB－197の130℃、190℃におけるG’、G”の周波数依存性曲線

（図3－5～8）…同一MFRにおける今月度測定試料と他プロセス重合品の粘弾性挙動の比較

図3－1より130℃におけるη^*の周波数曲線を今月度測定した試料について比較した。PTNシリーズについては測定周波数範囲内においてMFRに基づくと考えられる値の相違のほかは曲線は平行移動した形になっている。VIB－197は高周波数側と低周波数側の曲線の傾きの変化はPTNシリーズに比較して小さい。低周波数側の非ニュートン性はPTNシリーズに比較して大きくなっている。また、図3－2～4よりPTNシリーズ

の分子量が大きいことがわかる。
これらのデータより零剪断粘度、流動の活性化エネルギーを求めて表３－１にこれらの値をまとめた。

図３－５において本試料について同一ＭＦＲにおける９９％応力緩和時間を’９２／８月度に検討した試料と比較した。この図よりＰＴＮ－４４、７１は概ねＨＩＰ法LLDPEと同じレベルにあると考えられ、ＶＩＢ－１９６は以前の検討におけるＴＮ系触媒重合品と同じレベルにあると考えられる。

図３－６は同一ＭＦＲにおける零剪断粘度について比較した図である。この図より、同一ＭＦＲにおける零剪断粘度についても、ＰＴＮ－４４、７１は概ねＨＩＰ法LLDPEと同じレベルにあると考えられ、ＶＩＢ－１９６は以前の検討におけるＴＮ系触媒重合品と同じレベルにあると考えられる。

図３－７は同一ＭＦＲにおける流動の活性化エネルギー（ＦＡＥ）を比較したものである。ＰＴＮシリーズのＦＡＥは２０～３０KJ／molKとLLDPEとほぼ同じ値を示している
ＶＩＢ－１９６は４３KJ／molKとＬＤＰＥとほぼ同じ値を示している。

図３－８は同一ＭＦＲにおけるPower law index を比較したものである。ＰＴＮシリーズの値はおおよそ0.47であり、ＨＩＰ法LLDPEにおけるＭＦＲとPower law indexの関係を直線に近似した場合この直線より上にあり、また、図３－５～７の結果を考えあわせるとこの関係においてもＨＩＰ法LLDPEと同じレベルにあると推定される。また、ＶＩＢ－１９６は以前に測定したＴＮ系触媒重合ＰＥと同じレベルにあると推定される。

以上の結果より、今月度測定したslurry法ＴＮ触媒重合ＰＥおよびメタロセン系触媒重合ＰＥは前回までに測定したＨＩＰ法ＬＬＤＰＥと類似の粘弾性挙動を示し、ＴＮ触媒系を用い、かつＨＩＰ法と同様の重合条件で製造したＰＥは、ＦＡＥ以外の今回得られた粘弾性データより、以前に測定したＴＮ触媒重合ＰＥと構造的に大きな違いがないと推定される。

ＦＡＥはポリマーの分岐構造と大きな関連性があると考えられており、応力緩和挙動、零剪断粘度の結果を考え合わせるとＴＮ系触媒重合品はＨＩＰ法LLDPEより大きなＦＡＥの値を持つと推定される。この推定より、以前に測定したＴＮ系触媒重合ＰＥのＦＡＥについては重ねあわせ時の誤差などもふくめてさらに詳細に見直す必要があると考えられる。

4、今後の予定

1）　ＴＮ触媒重合品のＦＡＥの検討
2）　配向結晶化の粘弾性的検討

以上

Table Viscoelastic properties of PE obtained by novel catalyst
表３－１　新規触媒重合ＰＥの粘弾性的性質

試料名 Sample	MFR	T99(sec)	η0(P)	FAE(KJ/molK)	m
ＰＴＮ－４４	0.41	2.81	6.02E5	26.4	0.478
ＰＴＮ－７１	0.34	3.35	9.50E5	26.5	0.474
ＶＩＢ－１９６	2.85	3.63	2.75E5	44.5	0.557

m： Power law index (10～100rad/sec)

(図3-1) Freq● Sweep 1 (Temp = 130 ●)

Fig.3-1

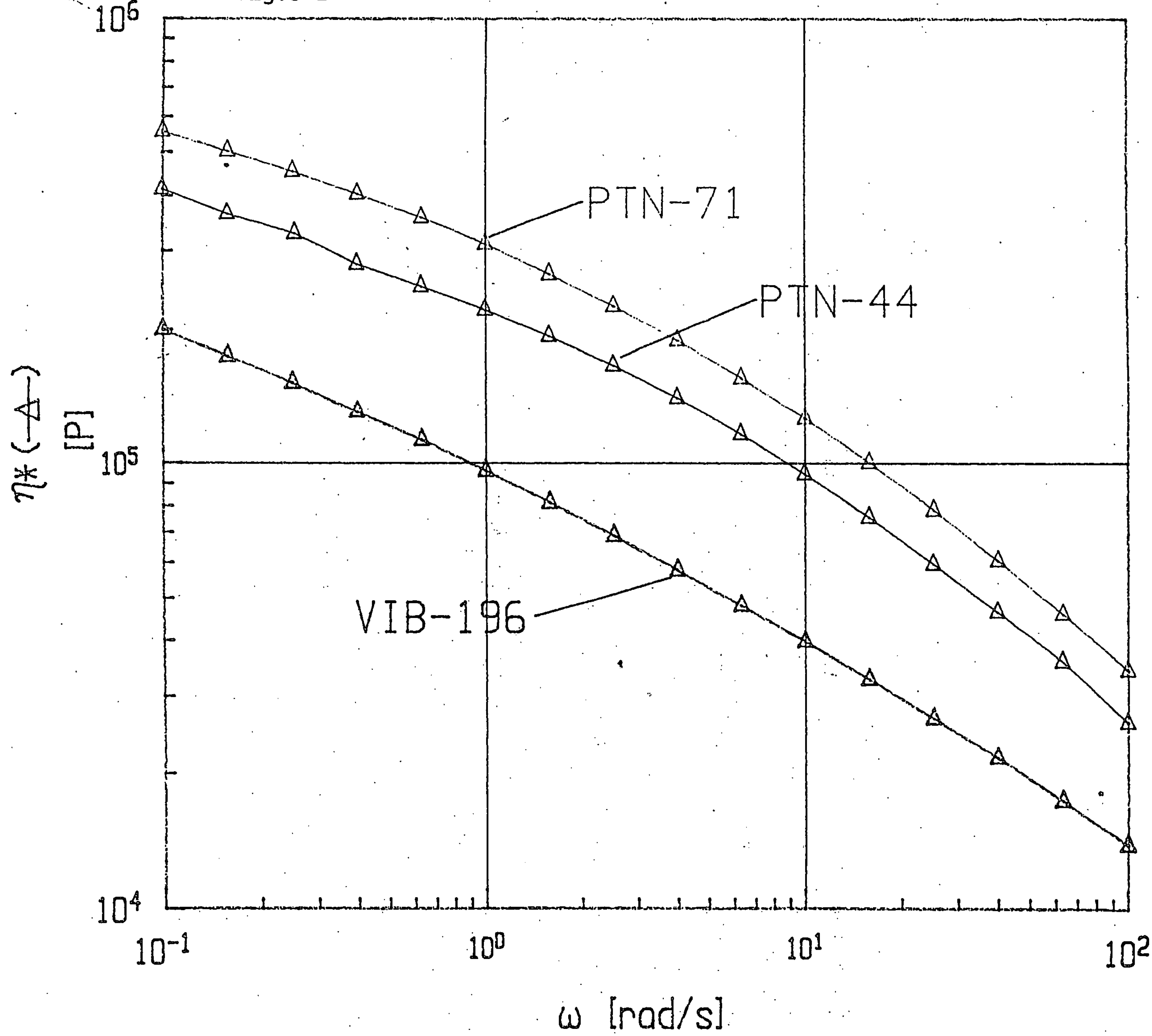


Fig.3-2

(図3-2) PTN-44 FREQ. SWEEP

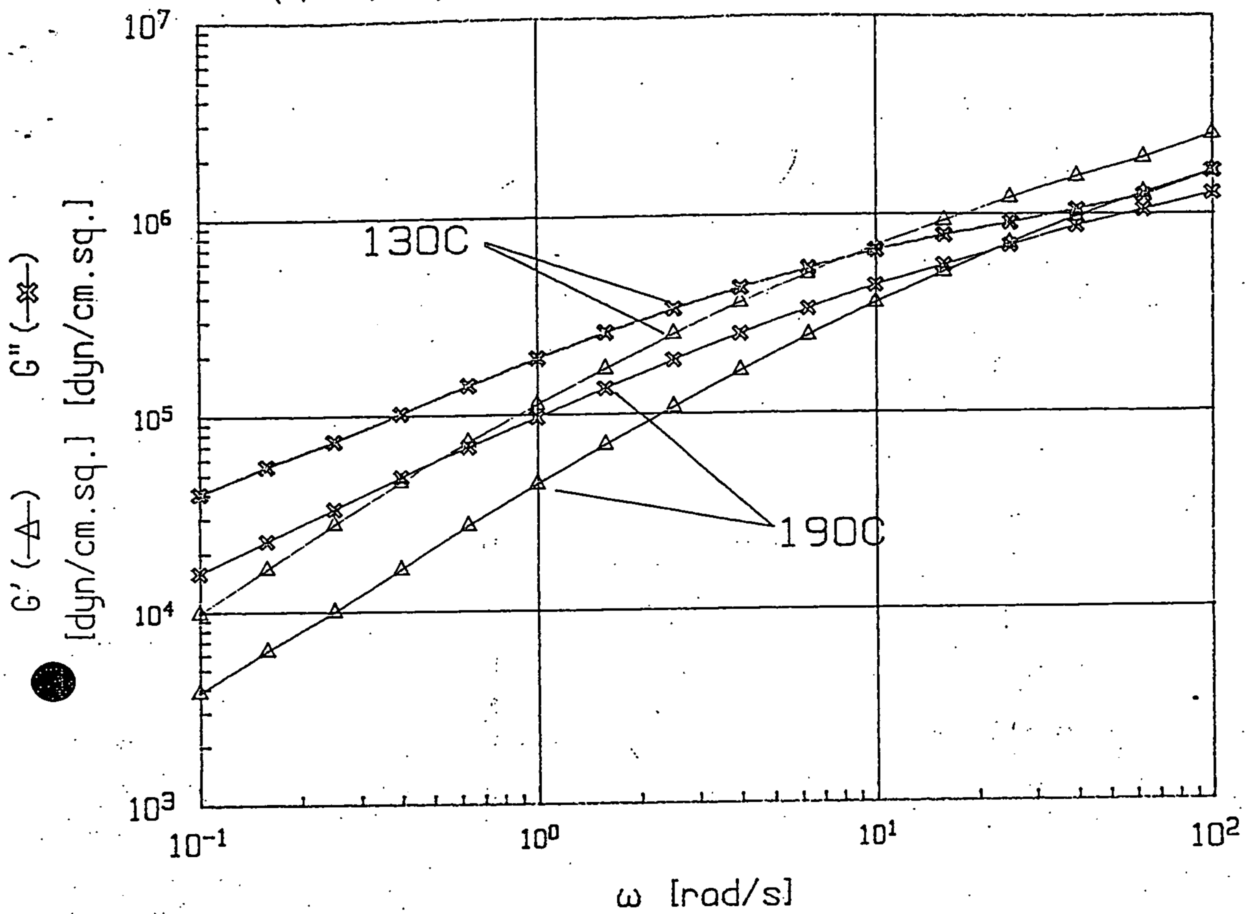


Fig.3-3

(図3-3) PTN-71 FREQ. SWEEP

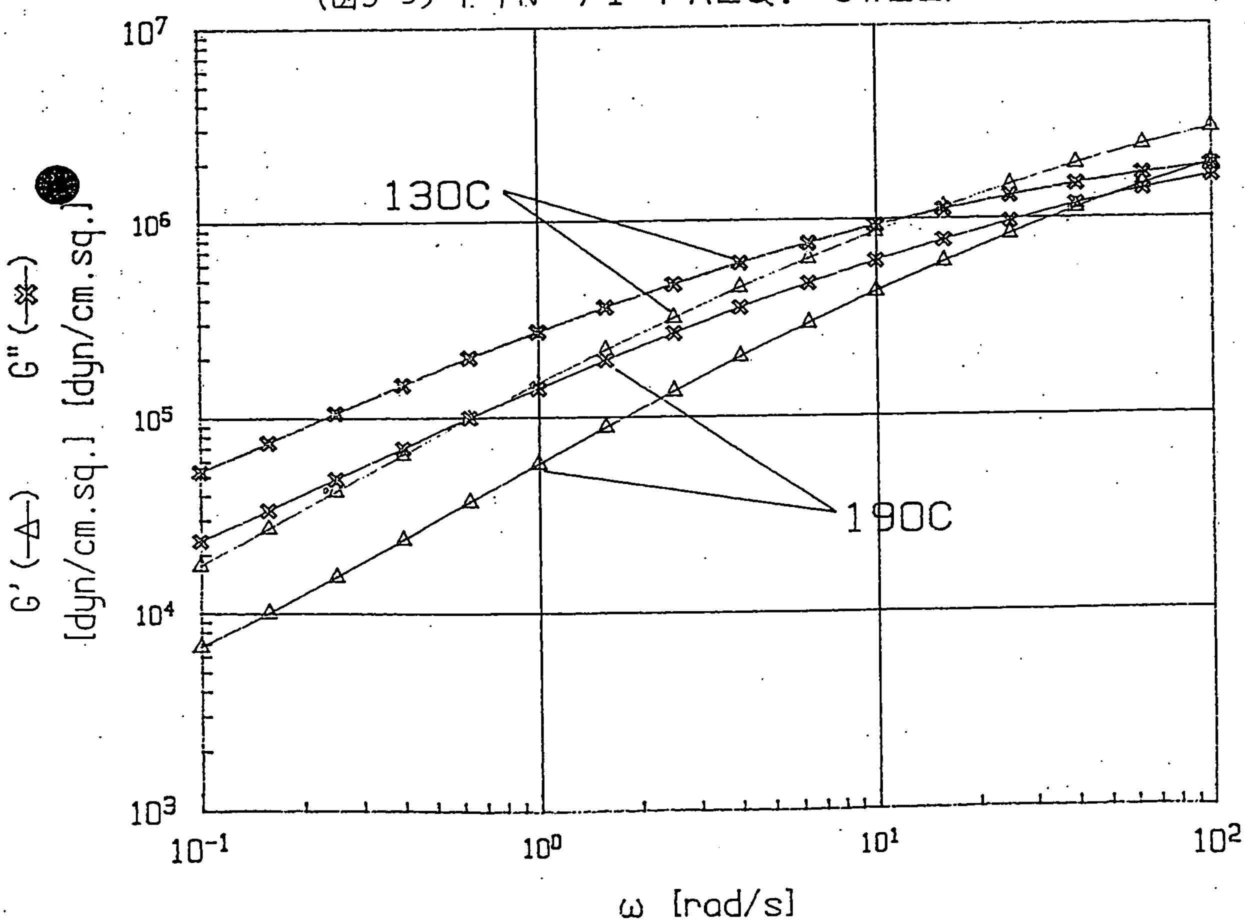
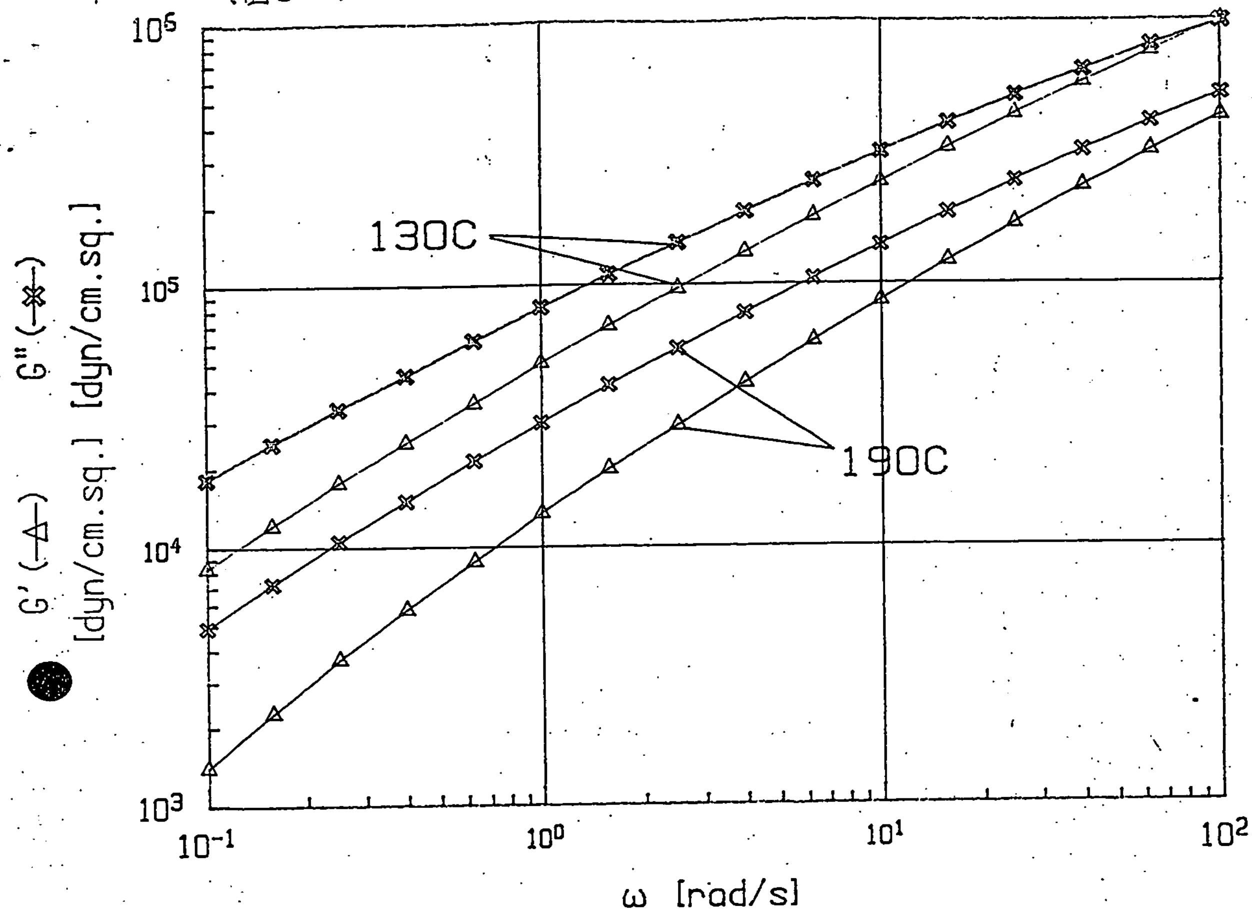
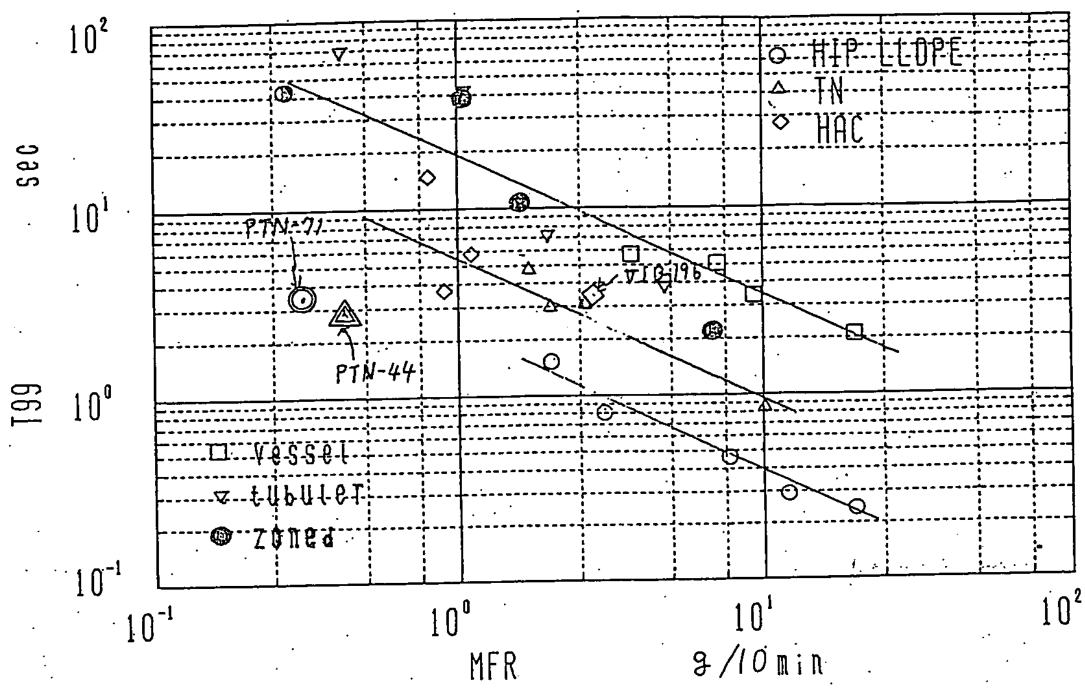


Fig.3-4

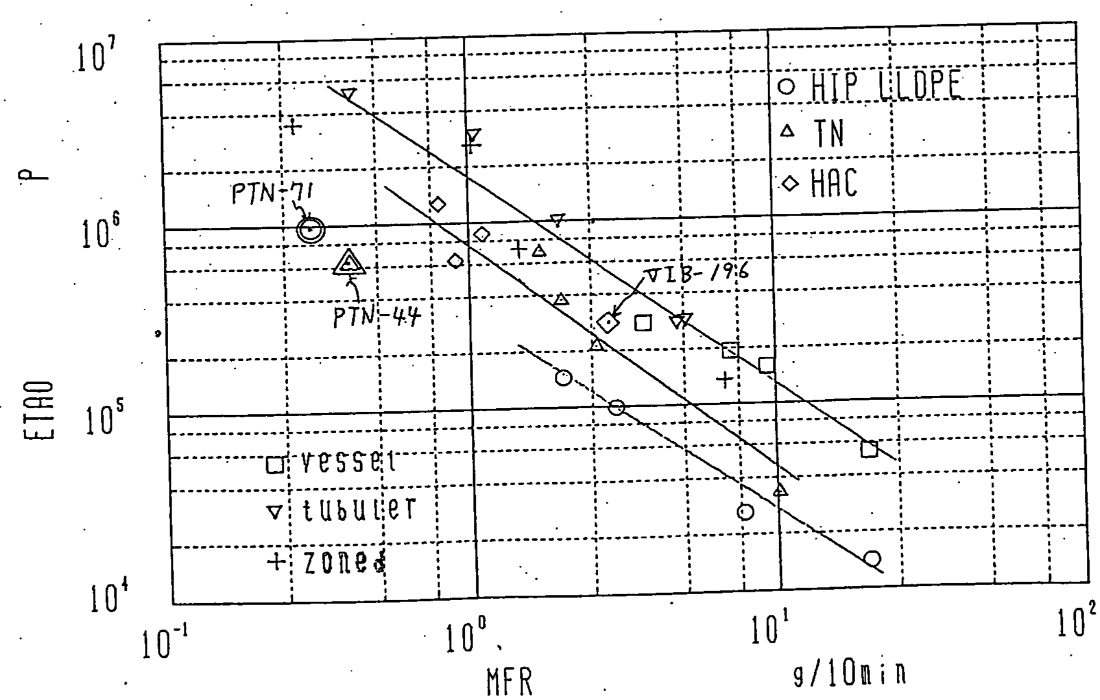
(図3-4) VIB-196 FREQ. SWEEP





(図3-5) MFRと99%緩和時間

(Fig.3-5) MFR and 99% Relaxation Time

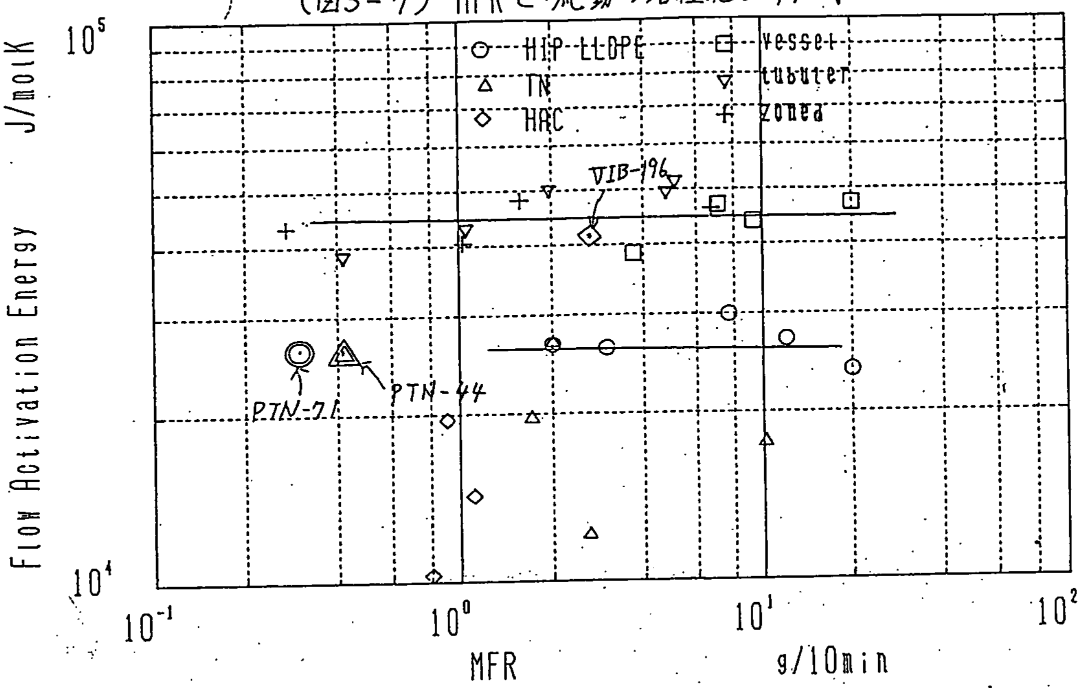


(図3-6) MFRと零セン断粘度

(Fig.3-6) MFR and Zero Shear Viscosity

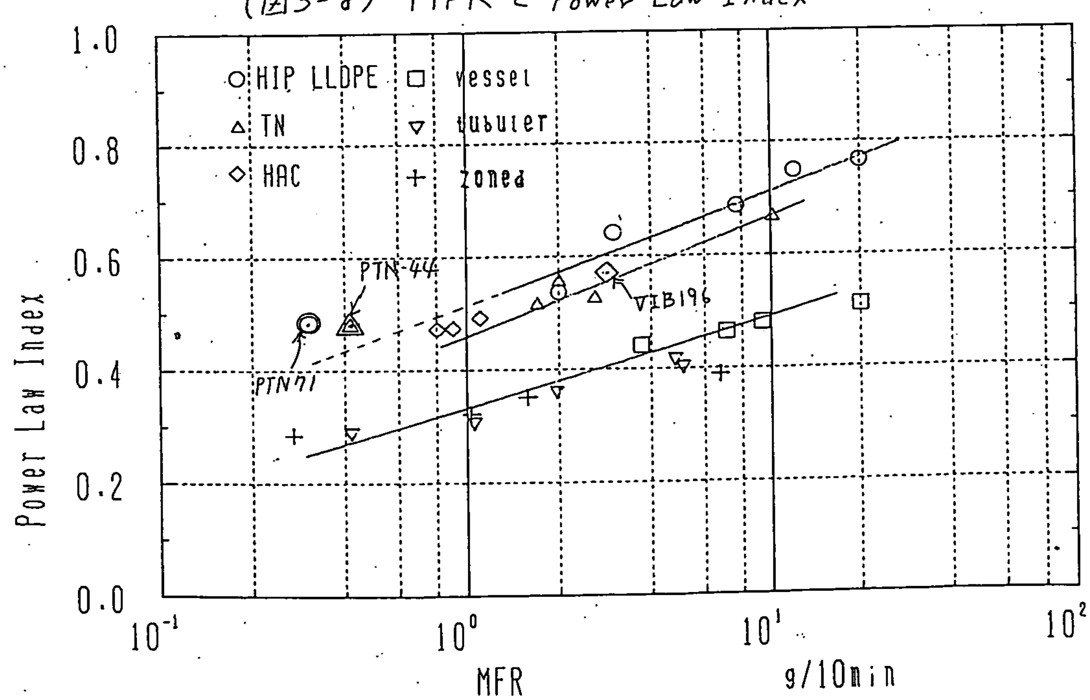
(Fig.3-7) MFR and Activation Energy of Flow

(図3-7) MFRと流動の活性化エネルギー



(Fig.3-8) MFR and Power Law IndeX

(図3-8) MFRとPower Law Index



[ENGLISH TRANSLATION]

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RESEARCH MONTHLY REPORT OF JANUARY Jan. 28, H5(1993)

KANDA

Research relating to structure and physical properties of polyethyelene

Behavior of dynamic viscoelasticity of PE polymerized by TN catalyst

1. Introduction

Dependencies on frequency of dynamic viscoelasticity of PE obtained by a slurry method using TN catalyst, PE obtained HIP method and PE polymerized by a Ti-based metallocene catalyst, were measured, and difference in viscoelasticity between these PEs' and PEs' which have been obtained by various processes, was compared.

2. Experiment

Sample	process	Me/1000C	MFR	MFRR
PTN-44	TN-4/DEAC/BEM(slurry)	18.2	0.41	31.4
PTN-71	Metallocene/DEAC/BEM	20.8	0.34	35.4
VIB-196	TN-4/DEAC/BEM(HIP)	14.9	2.85	45.1

Metallocene:Cp2Ti(Noct2)2

(Measurement)

1) Dependency on frequency of viscoelasticity

RMS-800 parallel plate strain: 20%

Temperature: 130℃→250℃(temp-freq. sweep)

Frequency 100→0.1 rad/sec

2) Stress relaxation test

Parallel plate, strain: 20%

Temperature: 130℃

3. Result and consideration

(Table3-1)………Summary of Viscoelasticity behavior of PTN-44, 71 and VIB-196

(Fig.3-1).........Frequency dependence curve of η* at 130℃ of PTN-44, 71 and VIB-196

(Figs.3-2~4) Frequency dependence curve of G' and G" at 130℃ and 190℃ of PTN-44, 71 and VIB-196

(Figs3-5~8) Comparison in viscoelasticity behavior of the samples measured this month with polymers obtained by other process having the same MFR as in said samples.

Frequency dependence curves of η* at 130℃ of samples measured this month were compared by showing them in Fig.3-1. (Omitted)

Change of slope of the curve between higher frequency side and lower frequency side of VIB-196, is small compared to those of PTN series. Newtonian property of the lower frequency side become large compared to PTN series. Further, it is found that the molecular weight of it is larger than those of PTN series from Figs 3-2~4.

A zero shear viscosity and activation energy of flow were determined from these data and values thereof were summarized in Table 3-1.

In Fig. 3-5, a 99% stress relaxation time of VIB 196 sample was compared to that of a sample in the same MFR, studied in August, 1992. From this figure, it is considered that PTN-44 and -71 are located generally at the level of LLDPE by a HIP method, and that VIB-196 is located at the level of polymer obtained using TN-type catalyst previously studied.

Fig. 3-6 is a drawing comparing the zero shear viscosity of samples in the same MFR. From this figure, it is considered that PTN-44 and -71 are located generally at the level of LLDPE by a HIP method, and that VIB-196 is located at the level of polymer obtained using TN-type catalyst previously studied.

In Fig.3-8, the activation energy of flow(FAE) of the samples in the same MFR is compared. FAEs' of the PTN series show

about the same values as that of LLDPE, as 20 to 30 kJ/mol K. VIB-196 shows about the same as that LDPE as 43 kJ/mol K.

From the above results, it is estimated that PE obtained by a slurry method of TN catalyst and PE polymerized by the metallocene catalyst show a viscoelastic behavior similar with the HIP method LLDPE, further, PE obtained under the same conditions as those in the HIP method using TN-type catalyst does not have large difference from the PE polymerized by TN catalyst from the viscoelasticity data obtained this month except FAE.

It is considered that FAE has a large relationship to a branch structure of a polymer, and it is estimated that polymer obtained by a TN series catalyst has a value of FAE larger than that of HIP method LLDPE when results of shear stress behavior and zero shear viscosity are additionally considered.

From this estimation, it is considered that detailed review, including a superposition error, of FAE previously measured of PE obtained by TN series catalyst is further required.

4. (Omitted below)

That's it.

報　告　要　旨

分類	2004-03

項　目	エチレン系新規ポリマーの開発	第1研究室	主任印
		報告者	重松裕二
副項目	均一組成分布エチレン－オレフィン共重合体の開発		

経緯）５研においてＴＮ触媒の高活性化が進み、HIP(CPK)での重合テストが行われた。この中で活性・基本物性・量等の面で良好な試料(VIB196)が得られたので評価を開始した。

５研の評価では、Ash が多く分岐に対する密度が高目であることから、物性評価の前に脱灰処理が必要であることがわかっていた。

試料）VIB196　　触媒：（TN4／DEAC）／BEM
重合条件：~~図~~表4
活性：2.35T/mol-Ti　（ZKP:3.25T/mol-Ti　[230℃]）

脱灰１）粉砕 → HCl-EtOH-水溶液（70℃）で洗浄・再沈
Ash分析結果：図５　脱灰効果きわめて小さい

物性）VIB196及びその脱灰１処理品の物性を表１に示す。比較はFA201-0を用いた。また、組成分布，DSCｻｰﾓｸﾞﾗﾑ，分子量分布の比較をそれぞれ図１～３に示す。

共通点（TN4/HIP:VIB161[表２]）
MFRR 大、SR 大、MTV 小、ﾒﾙﾄﾃﾝｼｮﾝ 大、分子量分布 広
その他の特徴：
組成分布 狭、ﾍﾌﾟﾀﾝ抽出率 少、ﾄﾗﾝｽﾋﾞﾆﾚﾝ割合 小
強度：
ﾃﾝｻｲﾙｲﾝﾊﾟｸﾄ 小、抗張力(US) 小　（Ashの影響が懸念される）

脱灰２）ｷｼﾚﾝに溶解 → HCl-EtOH-水溶液で再沈
本脱灰品については、密度，曲げ剛性率，ﾃﾝｻｲﾙｲﾝﾊﾟｸﾄ を測定中。（試料10g）
物性評価後 Ash分析を行う予定。

臭気定量）TN触媒特有のアミン臭の問題について、高活性化によるレベル低減が計られてきている。今回得られたVIB196は、VIB161に比べそのレベルは低い様子である。そこで触媒成分であるｼﾞｵｸﾁﾙｱﾐﾝ を用い

詳細資料No	

て両者のVM分析を試みた。

しかしながらGC分析において、現行の条件ではｱﾐﾝのカラムへの吸着あるいは沸点が高い(300℃弱)ためにVM成分として出てこない等の理由で測定困難であった。またﾌｨﾙﾑ加工時程度の温度(～200℃)でのペレットからの追い出しは、PEの融解及び分解を伴うために現行の分析技術の範囲外であるとのこと。

THF溶媒中で超音波抽出後のGC分析は可能であったが[1]、活性と臭気の関係付けによる必要活性レベルの推定はできない。

フィルム物性評価）Ash分析結果のAlの量からCl量を計算し、必要な中和剤(CaSt)添加量を求めたところ、最低12000ppm必要であることがわかった。ﾌｨﾙﾑ物性を評価する場合、CaSt添加量がかなり高くなり物性への影響も心配されることから現在ﾌｨﾙﾑ加工を見合わせている。

参考資料）

1) 1研試験報告書 No.92266

* HCl-EtOH-水溶液 -aqueous solution
0.3% HCl : EtOH = 1:9

Table 1 Evaluation of physical properties of TN catalyst CPK(HIP) high pressure polymerization test sample

表1

TN触媒CPK(HIP)高圧重合テスト品物性評価

Measurement item 測定項目		試料名 Sample	VIB196 (TN4/HIP)	VIB196 (粉砕・洗浄) (Pulverization・washing)	FA201−0 EGL178
MFR		(g/10min)	2.85	2.79	1.89
MFRR			45.1	44.6	26.0
SR			1.52	1.48	1.14
密度 Density		(g/cm^3)	0.9275	0.9276	0.9177
曲げ剛性率 Flexural rigidity		(kg/cm^2)	1910〜3020	2720	1790
テンサイル・インパクト Tensile impact		(kg・cm/cm^2)	109	96	632
引張特性 Tensile property	YS	(kg/cm^2)	133	134	105
	US	(kg/cm^2)	132	124	253
	UE	(%)	750	720	830
Melt Extensibility 150℃	MTV	(m/min)	61	61	115
	テンション	(g)	3.3	3.5	1.8
ヘプタン抽出率 Heptane-extracted rate		(wt%)	0.60	−	1.04
CXS		(wt%)	1.78	1.59	3.88
CH_3		(1000C)	14.9	14.3	18.9
C=O		(2000C)	−	−	0.07
RCH=CHR'		(2000C)	0.15	0.15	0.11
$RCH=CH_2$		(2000C)	1.40	1.32	0.92
$RR'C=CH_2$		(2000C)	0.15	0.06	0.27

VIB196:(TN4/DEAC)/BEM HIP(210℃)

ヘプタン抽出:粉砕品 50g×30℃×24hr

洗浄:70℃ HCl-EtOH-水溶液（脱薄黄色）

引張特性:引張速度500mm/min

Heptane-extracted: Pulverized product 50g x 30℃ x 24hr

Washing: 70℃ HCl-EtOH-aqueous solution (Discolored light yellow)

Tensile property: Tensile speed 500mm/min.

表2 物性測定記録　再掲

試料名			VIB159 ZKP/TiBA+EASC	VIB161 TN-4/TEA	VIB162 TN-4/TEA
基本物性	MFR (g/10min)		12.0	2.61	10.1
	MFRR		23.6	42.4	36.7
	SR		1.08	1.60	1.49
	密度 (g/cm³)		0.9193	0.9359	0.9312
	DSC	融解温度 (℃)	104.6, 119.2, 122.6	122.5	112.4, 119.8
		結晶化温度 (℃)	94.8, 107.7	111.6	108.8
	引張特性	YS (kg/cm²)	104	185	157
		US (kg/cm²)	145	121	98
		UE (%)	620	600	230
	曲げ剛性率 (kg/cm²)		1890	4370	3330
	引張衝撃強度 (kgcm/cm²)		130.8	93.5	59.2
	ビカット軟化点 (℃)		89.6	111.6	100.7
	ESCR[100℃, 1hr] (hr)		42	25	2.8
	Melt Extensibility	MTV (m/min)	209以上	41	174
		メルトテンション (g)	0.3	4.9	1.1
	ブラベンダ (160℃)	トルク (g·m)	750	1340	760
		樹脂温度 (℃)	166	177	167
	[η] 135℃ (dl/g)		1.002	1.227	0.998
	ヘプタン抽出率[粉砕] (wt%)		1.69	0.95	1.70
	CXS (WT%)		3.94	1.03	2.25
	GPC	Aw	3004	4083	3048
		An	1034	918	640
		Aw/An	2.9	4.4	4.8
赤外分析	SCB (/1000C)		20.5	9.8	13.7
	C=O (2000C)		0	0.021	0.017
	RCH=CHR' (2000C)		0.145	0.960	1.499
	RCH=CH₂ (2000C)		1.019	1.014	1.079
	RR'C=CH₂ (2000C)		0.453	0.220	0.278

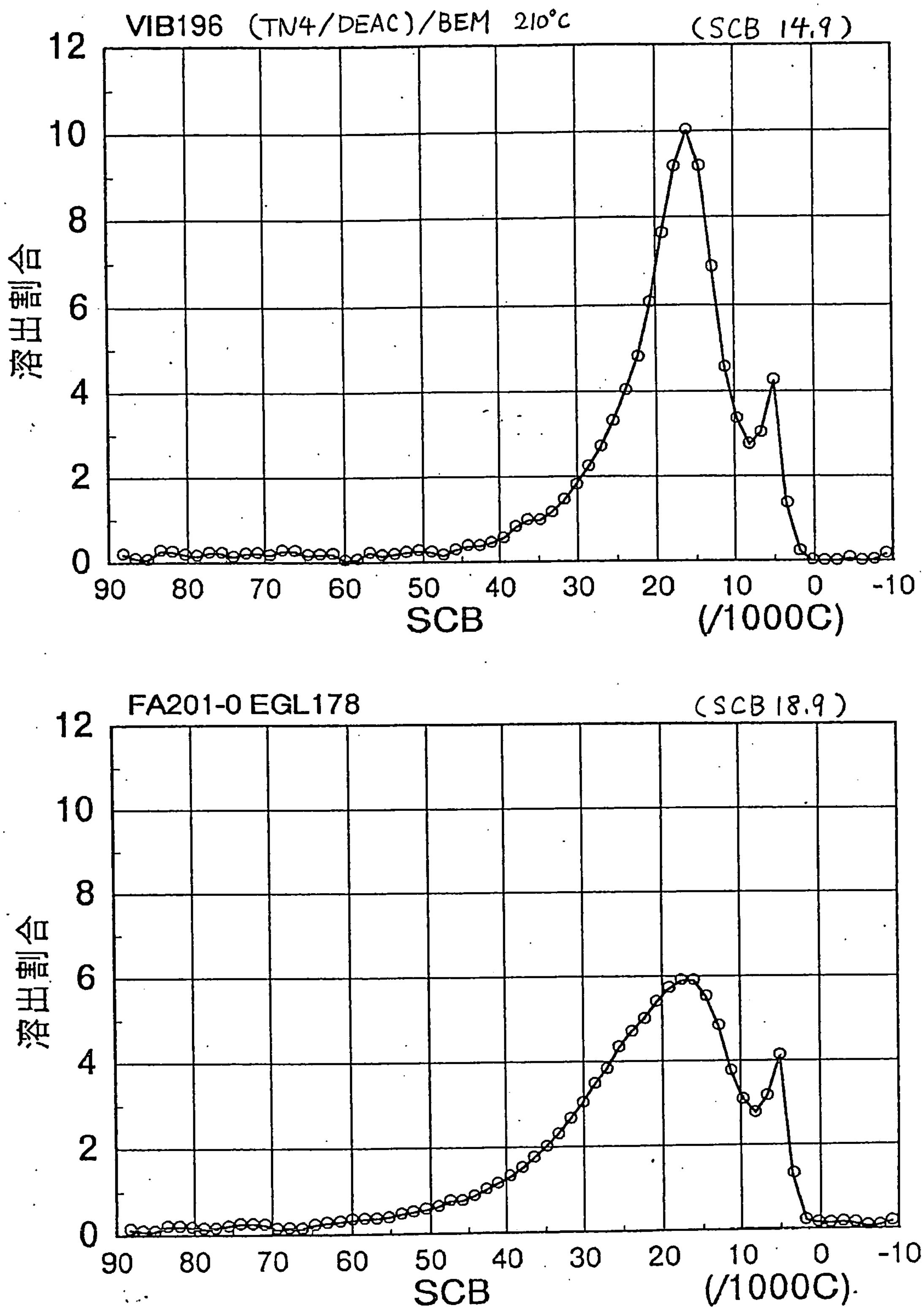
VIB196 (TN4/DEAC)/BEM 210°C
(SCB 14.9)
溶出割合
SCB
(/1000C)
FA201-0 EGL178
(SCB 18.9)
溶出割合
SCB
(/1000C)

図1、組成分布の比較

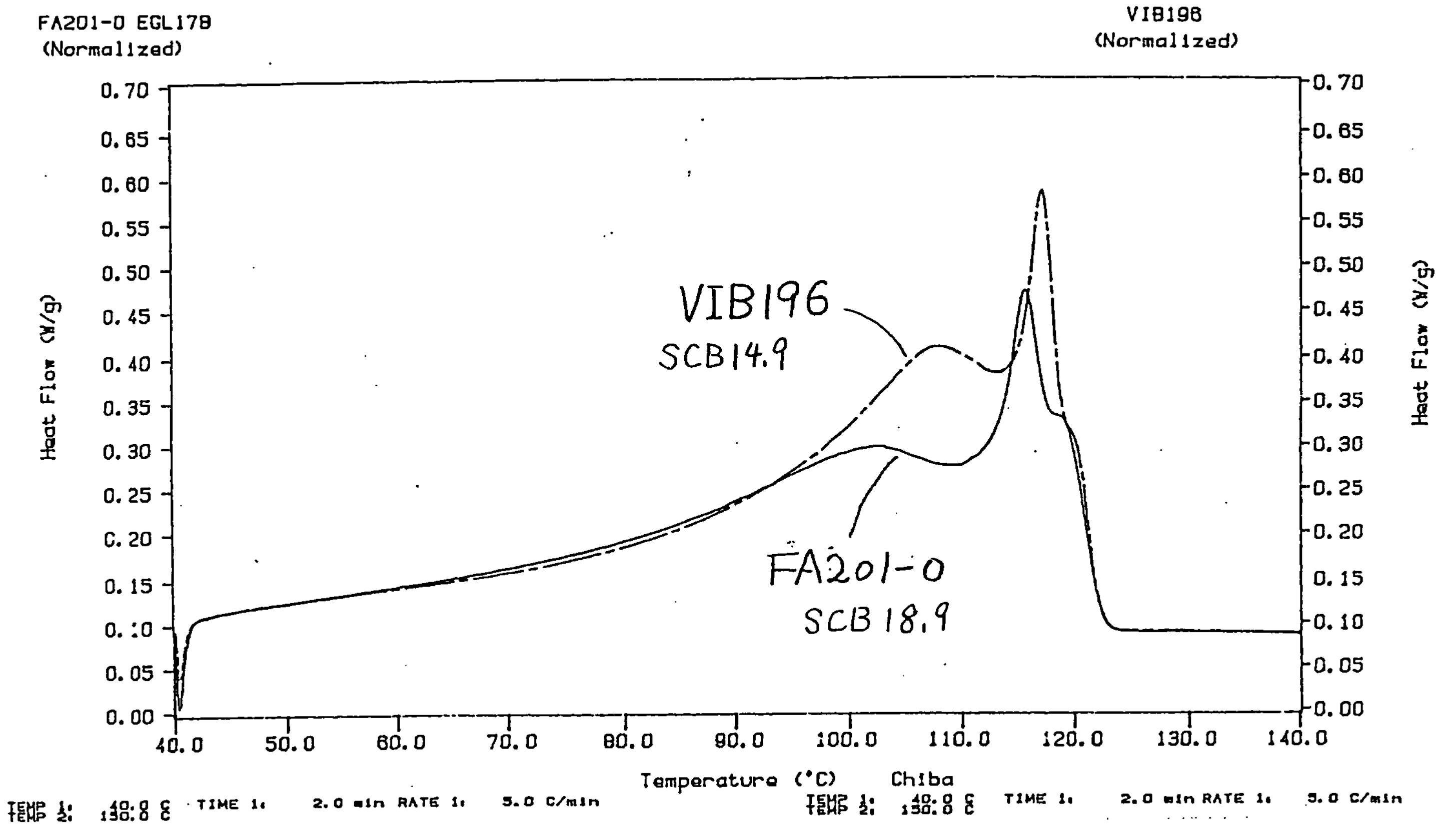

図2　DSCサーモグラムの比較

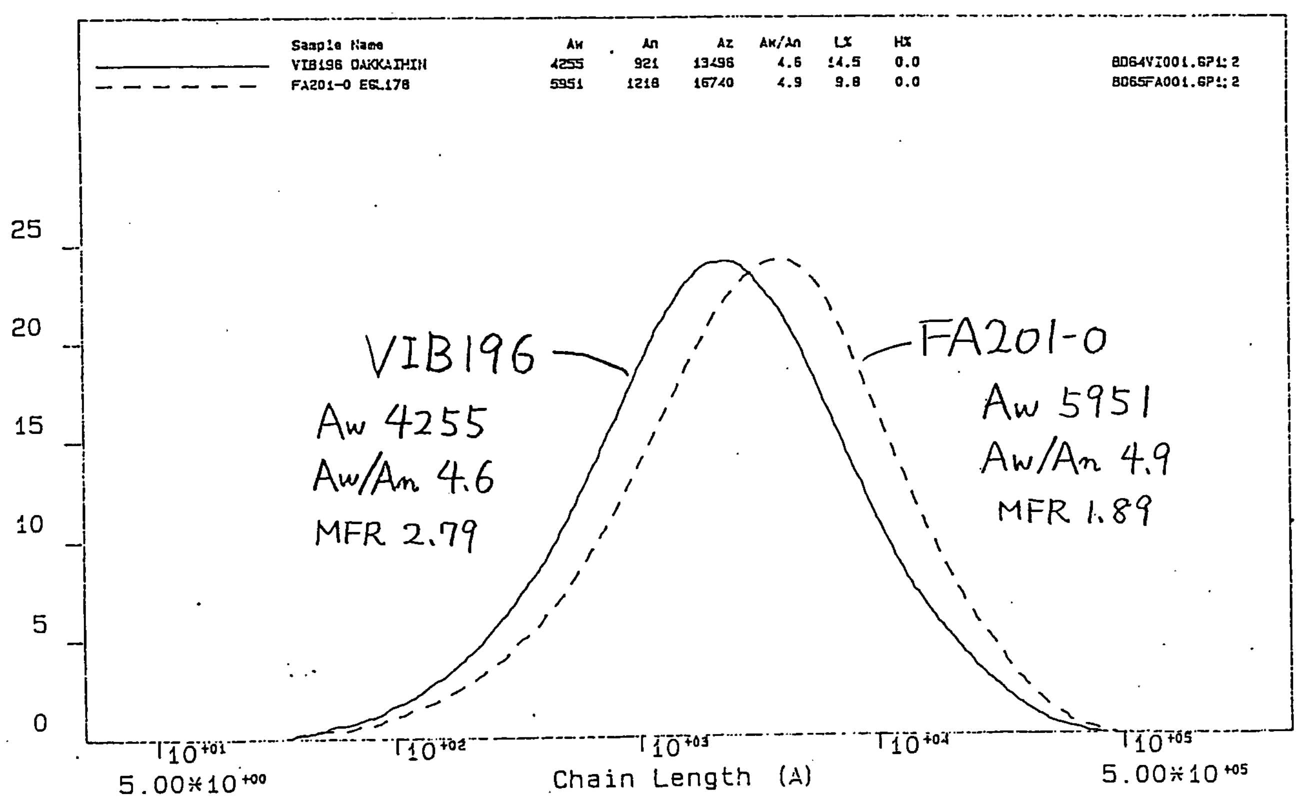

図3　分子量分布の比較

実験番号 VI -NO.			VIB-198
運転期間			11/28/ 1～28/23
解析期間			11/28/14～28/23
目的 条件	Y触媒		TN-4 2,5μﾓﾙ/G
	X1触媒		DEAC 315 μﾓﾙ/G
	X2触媒		BEM 69.6 μﾓﾙ/G
	ｺﾓﾉﾏｰ		ﾌﾞﾃﾝ
	目的		最高活性ﾚｼﾋﾟｰ探
			索
			AL/MG=4.5
			MG/TI=27.8
			AL/TI=126
Y触媒調合	種類		TN-4+DEAC
	濃度	μﾓﾙ/ｸﾞﾗﾑ	2.5
	DEAC	μﾓﾙ/ｸﾞﾗﾑ	315
	触媒ﾎﾟﾝﾌﾟ ｼｸﾞﾅﾙ %		21.8±0.06
			ﾅｼ
	TN-4	G/HR(MMOL/HR)	409(1.02)
	DEAC	G/HR(MMOL/HR)	409(129)
X触媒	X2種類		BEM
	[X2]	μﾓﾙ/ｸﾞﾗﾑ	69.6
	FX2	G/HR(MMOL/HR)	432(30.1)
Z触媒	種類		ﾅｼ
	[Z]	μﾓﾙ/ｸﾞﾗﾑ	
	FZ	G/HR(MMOL/HR)	
ｴﾁﾚﾝ	供給	KG/HR	8.17±0.06
	温度	℃	-27.3±0.1
水素	供給	G/HR	
ｺﾓﾉﾏｰ	種類		1-ﾌﾞﾃﾝ
	供給	KG/HR	10.41±0.03
重合条件	[H2]	ﾓﾙ-%	ﾅｼ
	[COM]	ﾓﾙ-%	38.9
	AL/MG	ﾓﾙ比	4.28
	MG/TI	ﾓﾙ比	29.4
	AL/TI	ﾓﾙ比	126
	AL/TI	ﾓﾙ比 灰分ﾍﾞｰｽ	
	R-110	SH加熱	16/16/16/16
	[ｷﾗｰ]	MMOL/G-SOL	10.85
	ﾌｨｰﾄﾞ	G/HR(ﾓﾙ/HR)	78(0.84)
	K/X+Y	ﾓﾙ比	5.3

反応制御	圧力	KG/CM^2-G	702±0
	供給	℃	18.3±0.2
	ﾄｯﾌﾟ	℃	174.9±0.7
	ﾐﾄﾞﾙ	℃	197.6±0.3
	制御	℃	210.6±0.5
	ﾗｲﾝ	℃	192.8±0.8
	PCV	℃	181.3±1.4
	E-120/121 SH加熱		16.0/18.6
D-130	入口	℃	199±0.3
	樹脂	℃	215.4±0.7
	ガス	℃	201.4±3.1
	吐出	KG/CM^2-G	
	ﾒｲｸ	KG/HR	2.41±0.13
	活性	ﾄﾝ/ﾓﾙ	2.35
	T-ASH	MG/KG (計算)	3,300
分析	MFR	G/10分	2.44±0.33
	SR	-/-	
	MFRR	-/-	
	ﾒﾁﾙ	C/1000C	17±0.2
	密度	G/CC	0.9275±0.0004
	CXS	WT-%	
	灰分	MG/TI/AL MG/KG	
	活性	[TI]ﾍﾞｰｽ ﾄﾝ/ﾓﾙ	
取扱流体	ｴﾁﾚﾝ		P-110
	ｺﾓﾉﾏｰ		P-310
	Y触媒		P-220A TN-4/DEAC
	X触媒		P-220A BEM/ﾍﾌﾟﾀﾝ
	50 WT% ｴﾀﾉｰﾙ ｷﾗｰ		P-230B ｷﾗｰ
実験状況・試作終了時の点検結果			

VIB196 重合条件
(5石研)
~~図4~~ 表4

Ash分析結果

ppm	Ti	Mg	Al
洗浄前	16.2	280	1030
洗浄後	15.3	272	995

粉砕 → HCl-EtOH-水溶液

表~~図~~5

English translation

RESEACH MONTHLY REPORT OF DECEMBER, HEISEI 4 (1992)

Reporting Date December 28, Heisei 4(1992)

SUMMARY Class 2004-03

1st. Laboratory.
Reporter Yuji SHIGEMATSU

Item Development of Ethylene-based novel polymer

Sub-item Development of Ethylene-olefin copolymer of uniform composition distribution

Background) A high activation of TN catalyst proceeded, and a polymerization test by HIP(CPK) was carried out in 5th Laboratory. Since a sample (VIB 196) which was good in activity, basic properties, amount and the like, could be obtained in the test, evaluation thereof was started.

In the evaluation of 5th Laboratory, it was known that de-ashing treatment was necessary prior to the evaluation of physical properties since value of the density to branch became high due to much ash.

Sample) VIB196 Catalyst: (TN4/DEAC) / BEM

Polymerization Conditions: Table 4

Activity: 2.35T/mol-Ti(ZKP:3.25T/mol-Ti [230℃])

De-ashing 1) Pulverization → Washing with HCl-EtOH-aqueous solution(70℃) and re-precipitation

Result of ash analysis: Fig.5 De-ashing effect is extremely small.

Physical Properties) Physical properties of VIB196 and product after de-ashing of VIB196 are shown in Table 1. FA-201 was used for comparison. Further, compositions of those in distribution, DSC thermo gram and molecular weight distribution are respectively shown in Figs. 1 to 3.

Common points(TN4/HIP:VIB161[Table 2])

MFRR: large, SR: large, MTV: small, Melt tension: large, Molecular weight distribution: broad

Other characteristics Composition distribution: narrow, Heptane-extraction ratio: small, Rate of trans-vinylene: small

Strength Tensile impact: small, Ultimate stress(US): small (there is fear of influence of

ash.)

De-ashing 2) Dissolution in Xylene → re-precipitation with HCl-EtOH-aqueous solution

A density, flexural rigidity and tensile impact of this de-ash product are being measured. Ash analysis will be conducted after measurement of the physical properties.

Quantitative determination of odor

With respect to a problem of amine odor inherent to TN catalyst, lowering of the level has been tried by high activation. The level of VIB196 obtained herein seem to be lower compared to VIB161, and so VM analysis of both samples was tried using dioctylamine.

However, in GC analysis, the measurement was difficult by the reason why VM component did not come out because of adsorption of the amine to the column and high boiling point (lower 300℃) under the present conditions, and the like. Further, purging from pellet at about film processing temperature is beyond the current analytical techniques because of occurrence of melting or decomposition of PE. Though GC analysis in THF solution after ultrasonic extraction was possible, the required activation level can not be estimated by making the connection between activity and odor.

Evaluation of physical property of film

(Omitted below)

Experiment Number			VIB-196
Operation term			11/28/1～28/23
Analysis term			11/28/14～28/23
Purpose Condition	Y catalyst		TN-4, 2.5 μ mole/G
	X1 catalyst		DEAC 315 μ mole/g
	X2 catalyst		BEM 69.8 μ mole/g
	Co-monomer		butene
	Purpose		Search of most active recipe
			Al/MG=4.5
			MG/Ti=27.8
			Al/Ti=128
Y catalyst preparation	Kind		TN-4 + DEAC
	Concentration	μ mole/g	2.5
	DEAC	μ mole/g	315
	Catalyst pump Signal %		21.8± 0.08
			None
	TN-4	G/HR(MMOL/HR)	409(1.02)
	DEAC	G/HR(MMOL/HR)	409(129)
X catalyst	Kind of X2		BEM
	[X 2]	μ mole/g	69.6
	FX2	G/HR(MMOL/HR)	432(30.1)
Z catalyst	Kind		None
	[Z]	μ mole/g	
	FZ	G/HR(MMOL/HR)	
Ethylene	Feed	KG/HR	8.17±0.08
	Temp.	℃	-27.3±-0.1
Hydrogen	Feed		
Co-monomer	Kind		1-butene
	Feed	KG/HR	10.41±0.03
Polymerization Condition	[H2]	Mole%	None
	[COM]	Mole%	38.9
	AL/MC	Molar ratio	4.28
	MG/TI	Molar ratio	29.4
	AL/TI	Molar ratio	128
	AL/TI	Molar ratio, Ash base	
	R-110	SH heating	16/16/16/16
	[Killer]	MMOL/G-SOL	10.85
	Feed	G/HR(mole%/HR)	78(0.84)
	K/X+Y	Molar ratio	5.3

Reaction control	Pressure	KG/CM?2-G	702±0
	Feed	℃	18.3±0.2
	Top	℃	174.9±0.7
	Middle	℃	197.8±0.3
	Control	℃	210.6±0.5
	Line	℃	192.8±0.8
	PCV	℃	181.3±1.4
	E-120/121 SH heating		16.0±18.5
D-130	Inlet	℃	199±0.3
	Resin	℃	215.4±0.7
	Gas	℃	201.4±3.1
	Exhaustion	KG/CM?2-G	
	Make	KG/HR	2.41±0.13
	Activity	Ton/mole	2.35±
	T-ASH	MG/Kg(Calculation)	3,300±
Analysis	MFR	G/10 min.	2.44±0.33
	SR	-/-	
	MFRR	-/-	
	Methyl	C/1000C	17±0.2
	Density	G/CC	0.9275±0.0004
	CXS	WY-%	
	Ash	MG/TI/AL MG/KG	
	Activity	[TI]base Ton/mole	
Operated fluid	Ethylene		P-110
	Co-monomer		P-310
	Y catalyst		P-220A TN-4/DEAC
	X catalyst		P220A BEM/heptane
	50 wt% ethanol killer		P-2308 Killer
Experiment Condition/check result at the end of the test			

VIB-196 Polymerization condition

Table 4

Result of ash analysis

ppm	Ti	Mg	Al
Before washing	16.2	280	1030
After washing	15.3	272	995

Pulverization → HCl-EtOH-aqueous solution

Table 5